

The effect of surfactants on the distribution of organic compounds in the soil solid/water system

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Abstract

The efficiency of soil remediation by surfactant washing was evaluated via the measured distribution coefficients of a number of nonpolar compounds in several soil–water mixtures. The studied compounds (contaminants) are BTEX (benzene, toluene, ethylbenzene, and *p*-xylene) and three chlorinated pesticides (lindane, α -BHC, and heptachlor epoxide), which span several orders of magnitude in water solubility (S_w). A peat, and two natural soils were used that comprise a wide range in soil organic matter (SOM) content. The surfactants tested included cationic, anionic and nonionic types, with concentrations up to five to six times the critical micelle concentration (CMC). The K_d^*/K_d values were used to evaluate the remediation efficiency under various operation conditions. For relatively water soluble BTEX compounds, the surfactant adsorption on the soil surface is the deciding factor on contaminant desorption from soil. For the less-soluble pesticides, surfactant micelles in solution influence the contaminant desorption more. The contaminants partitioning to SOM or adsorbed surfactants lowers the desorption efficiency. Anionic surfactants are found to be a better choice on soil remediation because they do not form admicelle on soil surface that enhances the SOM content. Cationic surfactant, which adsorb onto soil surfaces, leads to poor remediation efficiency. An improper selection of surfactant would result in inefficiency in soil remediation by surfactant washing.

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1. Introduction

The problem of soil pollution has been widely recognized in recent years. How contaminated soil should be cleaned has become an important issue. Among the suggested remediation methods, the surfactant washing of contaminated soils has been a common approach [1–4]. Although surfactants can effectively remove excess nonaqueous-phase organic liquids (NAPLs) or solids from water or from subsurface, the efficiency of surfactants in systems where the contaminants are subsaturated is subject to system conditions [5,6]. One major reason that the surfactant washing can clean contaminated soils is that the surfactant solution can enhance the solubiliza-

tion of otherwise relatively insoluble organic compounds, especially at concentrations greatly exceeding the CMC [7,8]. An unsaturated contaminant system is of practical interest because most soils or sediments are contaminated by subsaturated levels of organic chemicals in natural environments.

Aside from this potential application, the surfactant in a contaminant–soil–water system may also complicate the contaminant interaction between soil and water. In a pure water and soil system, organic solutes only partition to the SOM, and the distribution coefficient K_d , i.e., the ratio of the solute to the soil and to the solution, can be expressed as follows:

$$\frac{x}{m} = K_d C \quad (1)$$

where x is the amount of contaminant partitioned to soil (mg); m is the soil weight (g); C is the contaminant concentration in a solution at equilibrium (mass/volume). In this case, K_d is a function of the contaminant (solute) solubility and the SOM.

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However, the SOM content may vary with surfactant adsorption onto soil. The level of SOM in soil has an impact on the contaminant distribution between soil (or a natural solid) and water [9]. Contrary to the effect of SOM on contaminant sorption, the surfactant in water may enhance the contaminant solubility. One latter effect is expressed by Lee et al. [9] as

$$\frac{S_w^*}{S_w} = 1 + X_{mn}K_{mn} + X_{mc}K_{mc} \quad (2)$$

where S_w is the organic solute solubility in water; S_w^* is the apparent solubility in the surfactant solution; X_{mn} is the concentration of the surfactant as monomer in water (mass/mass, dimensionless) ($X_{mn} = X$, if $X \leq \text{CMC}$; $X_{mn} = \text{CMC}$, if $X > \text{CMC}$); X_{mc} is the concentration (dimensionless) of the surfactant as micelle in water ($X_{mc} = X - \text{CMC}$); K_{mn} is the partition-like coefficient of the solute between surfactant monomer and water (dimensionless); and K_{mc} is the partitioning coefficient between the aqueous micellar phase and water (dimensionless).

As to the surfactant properties, the mass fraction (f_{sf}) of the soil-sorbed surfactant and the contaminant distribution coefficient between the sorbed surfactant and water (K_{sf}) are dominant factors on the apparent K_d . Thus, depending on the balance of the above-mentioned effects, the contaminant soil/solid–water distribution coefficient with a surfactant (K_d^*) may either decrease or increase relative to the distribution coefficient without the surfactant (K_d). The relation between K_d^* and K_d for a subsaturated contaminant in a soil/solid–water mixture, with and without a surfactant, has been established, which accounts for the contaminant levels in the solid and solution phases [5]:

$$K_d^* = K_d \frac{1 + f_{sf}K_{sf}/K_d}{1 + X_{mn}K_{mn} + X_{mc}K_{mc}} \quad (3)$$

In Eq. (3), the surfactant application generates two opposing effects [10]: (i) the surfactant sorbed to the soil increases the contaminant sorption; (ii) surfactant in solution promotes the contaminant solubility. The important features of Eq. (3) that need to be defined include: (i) the K_d value of natural soil or sediment; (ii) the extent of surfactant sorbed on the soil, f_{sf} ; (iii) the properties of the surfactant in the soil to K_{sf} ; (iv) the contaminant solubility enhancement by the surfactant, ($1 + X_{mn}K_{mn} + X_{mc}K_{mc}$).

The K_d value of a low-polarity organic solute without surfactants is determined primarily by the solute partitioning to the SOM, i.e., $K_d = f_{om}K_{om}$, where the f_{om} is the SOM fraction in the soil and K_{om} is the solute partition coefficient between the SOM and the water. Here, the adsorption of a low-polarity solute on the soil mineral matter is relatively insignificant because of the strong adsorptive competition of water.

2. Background

Unlike ordinary low-polarity solutes, many surfactants (e.g., nonionic and cationic ones) may adsorb efficiently onto certain soil minerals [10], supposedly due to their high polarities and large molecular weights. There are three possible mechanisms whereby surfactants to soils sorb: ion exchange, adsorption and surfactant partitioning to SOM. For cationic surfactants, ionic bonding is the main mechanism because soils often contain negative charges on the surface. For nonionic surfactants, the adsorption usually occurs due to hydrogen bonding or the van der Waals force. Surfactants may also partition into the SOM to an extent influenced by the properties of the surfactant and the SOM. The adsorption of anionic surfactants is similar to that for the nonionic surfactants, but the repulsive charge on the soil surface tends to weaken the adsorption. The sum of the above effects comprises f_{sf} in Eq. (3).

The surfactant micelles offer a good hydrophobic environment to which the organic solutes can partition. This is because a solute with a relatively lower S_w has a relatively high obvious affinity with the hydrophobic surfactant group. The K_{mn} term is small relative to the K_{mc} term, and the K_{mc} values have magnitudes similar to their K_{ow} values. Therefore, a homogeneous surfactant at $X < \text{CMC}$ will not significantly enhance the water solubility of organic compounds. It is worth mentioning that the magnitude of K_{sf} is not a direct function of f_{sf} , but rather a function of the aggregation state of the sorbed surfactant molecules. In principle, only an adsorbed surfactant can form a molecular aggregation, the extent being related to the amount adsorbed and the solid surface properties [11]. If surfactants partition only to SOM, the K_{sf} is equal to zero.

Although the interaction of the solute and the soil in the surfactant solution has been widely discussed [5,9,12–14], knowledge about the sorption of different surfactants to the complex soil mineral phase, the SOM and the aggregation state of the adsorbed surfactant are seriously lacking, thus prohibiting predictions of K_d^*/K_d from available system parameters. It is thus important to describe the differences in contaminant distribution between soil and water with various surfactant types and concentrations in the different soil–water systems.

In this work, the K_d and K_d^* values of the examined subsaturated organic compounds were measured in several surfactant–soil–water systems. The changes in K_d^*/K_d were then used to evaluate the performance of various surfactants with some soluble contaminants and soils that contain various SOM content. The selected contaminants were the four BTEX compounds (benzene, toluene, ethylbenzene, and *p*-xylene) and three pesticides (lindane, α -BHC, and heptachlor epoxide). The selected contaminants have a wide range of S_w and K_{ow} . The three types of surfactants included anionic sodium dodecylbenzene sulfonate (SDBS), cationic domiphen bromide (DB) and nonionic Triton-100 (TX-100). From an environmental standpoint, the findings from this

study with the applied surfactant levels should facilitate evaluation of the potential impact of this and similar surfactants on the contaminant distribution behavior in natural water and/or at waste-disposal sites.

3. Experimental

All of the experiments conducted in the laboratory for this paper are described below.

3.1. Chemicals

The four BTEX compounds (benzene, toluene, ethylbenzene, and *p*-xylene) were supplied by the Aldrich Company, Milwaukee, WI. The three pesticides, α -BHC (hexachlorocyclohexane, α -isomer), lindane (hexachlorocyclohexane, β -isomer), and heptachlor epoxide (HPOX), were obtained from the Riedel de Haën Company, Germany. All these compounds were of analytical grade or better and were used as received. Some of the physico-chemical properties of these compounds are given in Table 1. The three types of surfactants were supplied by the Riedel de Haën Company, Germany.

3.2. Soil pretreatment and properties

Three soils were selected for the sorption experiments. The soils used were a sandy loam soil from Taichung, Taiwan (designated as TCS), an organic-rich top soil from Shamao Mountain in Taipei County, Taiwan (designated as SMS), and a type of peat from the Everglades, FL (designated as FP). The peat is a reference sample from the International Humic Substances Society (IHSS). The soil samples were air-dried and then sieved to obtain particles of less than 2.0 mm, before all of the sorption experiments. For surface area determination, the soil and clay samples were outgassed at 135 °C prior to the measurement. The surface areas (SAs) were determined using a Brunauer-Emmett-Teller (BET) plot of the nitrogen adsorption data at the liquid nitrogen temperature using a

Table 1
Molecular properties of BTEX and chlorinated pesticides at 25 °C: MW = molecular weight, MP = melting point, S_w = water solubility, K_{ow} = octanol–water partition coefficient

Compound	MW	S_w (mg/L)	$\log K_{oc}$	$\log K_{ow}$
Benzene	78	1780 ^a	2.09 ^c	2.13 ^c
Toluene	90	515 ^a	2.85 ^c	2.69 ^c
Ethylbenzene	102	152 ^a	3.59 ^c	3.15 ^c
<i>p</i> -Xylene	102	185 ^a	3.48 ^c	3.15 ^c
Lindane	291	7.8 ^b	5.81 ^c	3.72 ^c
α -BHC	291	1.4 ^b	6.75 ^c	3.72 ^c
HPOX	389	0.35 ^b	7.68 ^c	4.97 ^b

^a As cited in ref [16].

^b Ref [6].

^c Estimated according to the method described in Ref [17].

Table 2
Properties of studied solid samples: SA = BET-(N₂) surface area (m²/g), f_{om} = fraction of organic matter in soils (%), and CEC = cation exchange capacity (meq/100g)

Soil	Abbreviation	SA	f_{om}	CEC	Texture
Taichung soil	TCS	10.2	2.40	3.40	Sandy loam
Shamou Mountain soil	SMS	6.8	11.0	44	Loam
Florida peat	FP	1.30	86.4	147	Peat

Quantasorb Jr. sorption apparatus, with helium as the carrier gas. The dry SAs and other properties of the solid samples are given in Table 2.

3.3. K_d^* and K_d analysis

The initial surfactant concentrations were set to reach to five to seven times nominal CMC in deionized water. The 0.1–1.0 g of the tested soil, determined by adding varying quantities of a given test compound, was mixed with 20 mL of the above-mentioned surfactant solution in Corex glass tubes, and then the target contaminants of about 30–60% S_w in the surfactant-soil mixture solution were added into the tubes. Although the partitioning of the organic compounds was assumed to have an insignificant competitive behavior, the experiments of the high- S_w BTEX and low- S_w pesticides were treated individually, for the analysis convenience.

Benzene and toluene were added directly as neat liquids, respectively, using 25- and 10- μ L Hamilton microliter syringes. The other compounds were added as stock solutions in methanol. The small amount of methanol in the water solution (<2%) was assumed to have an insignificant effect on the distribution of the tested compound, as has been found in similar studies on organic compound sorption on soils. After the above process, the tubes were closed with aluminum foil-lined screw caps and equilibrated for 48 h in a reciprocating shaker with 120 rpm. The resultant slurries were then centrifuged for 30 min at 8000 rpm (7649 \times g) to separate the solution and solid phases. Aliquots of the solution phase (2 mL) were then transferred into glass vials containing 10 mL of hexane (for lindane, α -BHC, and HPOX) or of carbon disulfide (for BTEX solutes). These vials were sealed with aluminum foil-lined screw caps and shaken for 2 h on a reciprocating shaker with 120 rpm. The distribution coefficients (K_d^*) of the compounds in the surfactant-soil–water mixtures were determined using extracts injected into GC. The intrinsic distribution coefficients of the compounds with the samples (K_d) were similarly measured without the addition of surfactant to the system. The amount of sorbed compound was determined using the difference in the initial and final concentrations. With Eq. (1), the K_d or K_d^* values were obtained via the linear regression using the various sorbed amounts and equilibrium concentrations.

Table 3
 K_d values of selected solutes in the different soil–water systems

Compound	TCS	SMS	FP
Benzene	1.17	5.11	8.33
Toluene	1.91	6.62	20.8
Ethylbenzene	3.93	11.7	51.2
<i>p</i> -Xylene	4.06	12.9	61.7
Lindane	12.3	136	923
α -BHC	20.4	246	1122
HPOX	121	783	3975

3.4. Analytical conditions

The GC analysis was performed on a Model 5890A Hewlett Packard gas chromatograph equipped with either an electron capture detector (for lindane, α -BHC, and HPOX) or a flame ionization detector (for BTEX compounds). A 5% sp-1200/1.5% Bentonite 34 on 100/120 Supelcoport packed steel column (1.8 m \times 3.2 mm i.d.) was used for separation for BTEX compounds; a 1.5% sp-2250/1.95% sp-2401 on 100/120 Supelcoport packed glass column (2.4 m \times 6.4 mm i.d.) was used for separation for the pesticides. Each experiment was duplicated and the data averaged. When the bias of the repeated experiments exceeded 15%, the triplicate repetitions were made. Blank experiments, without soil, were performed for the tested compounds; the recoveries ranged from 85 to 95%. Measured equilibrium concentrations were not adjusted for the recoveries.

4. Results and discussion

The K_d values for selected organic compounds in all soil–water systems without surfactants are listed in Table 3. Since the main mechanism for the sorption of NOC to the soil is in partition to the SOM, one will expect that the K_d values with the selected contaminants would increase with an increase in f_{om} , and for a specific soil K_d would decrease as S_w increases [18]. As expected, the K_d values are closely related to the f_{om} values consistent with solute partitioning to SOM as the primary process. In addition, the K_d values with a given soil follows the order: benzene < toluene < ethylbenzene < *p*-xylene < lindane = α -BHC < HPOX, as expected according to their lipophilic trend [10,13,19,20]. The unimportance of soil minerals can be ascribed to their strong adsorption of water, which suppresses NOC adsorption. However, when surfactants are added into the soil–water systems, the affinity of NOCs to soil minerals may change significantly because of the surfactant adsorption onto minerals. In addition, the surfactant adsorption on soils may also enhance the SOM content, thus reducing NOC level in water.

4.1. Effects of the different ionic surfactants

To evaluate the effects of different types of surfactants, we selected relatively water soluble BTEX ($S_w > 100$ mg/L) as

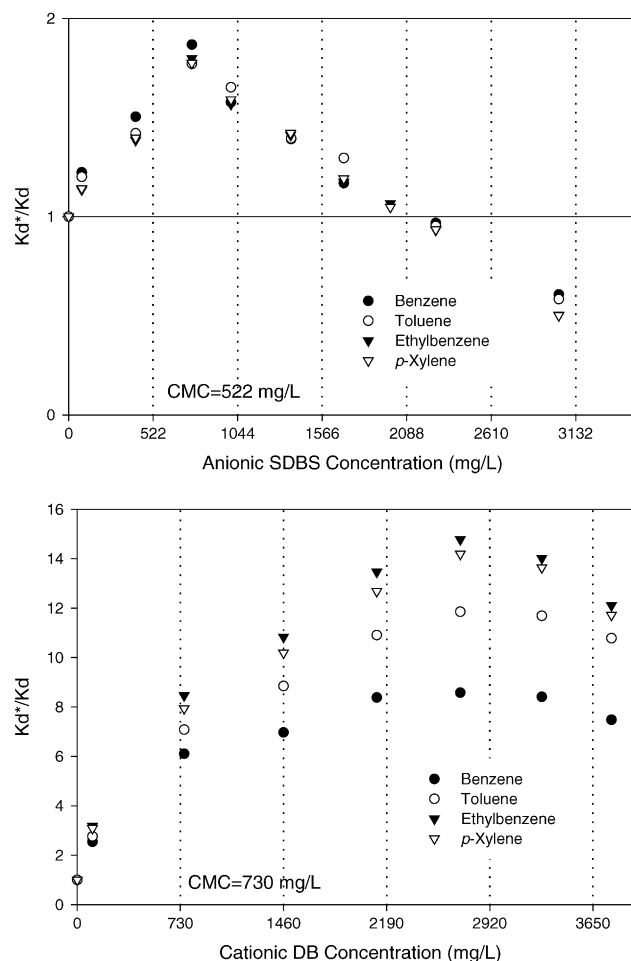


Fig. 1. Changes in K_d^*/K_d values of BTEX on TCS with SDBS and DB at the various added surfactant concentration.

the test compounds because they are frequently occur in natural environments. The impacts of cationic and anionic surfactants on the solute sorption were examined by determining the K_d values of the tested compounds using two kinds of natural soils under a wide range of surfactant concentrations. The K_d values in Table 3 vary widely between the tested compounds, and their normalized K_d^*/K_d values are used to define the remediation efficiency. If the K_d^*/K_d ratio exceeds one, the desorption of BTEX is considered to be inefficient for the system involved. Conversely, a ratio of less than one means that the soil remediation is favorable. The observed K_d^*/K_d values are indicated in Figs. 1 and 2. The K_d^*/K_d ratios for BTEX in anionic surfactant–soil–water systems show a general tendency towards maximum when the surfactant concentration is about one to two times the CMC. However, the maximum ratios for contaminants in the cationic surfactant system occur at four to five times the CMC. Because the anionic surfactant has a low tendency for admicelle formation, only adsorption of its hydrophobic groups on the soil surfaces via van der Waals force may occur. At the low surfactant concentrations, organic contaminants partition into the enhanced SOM (i.e. the adsorbed surfactant), leading to an increase in

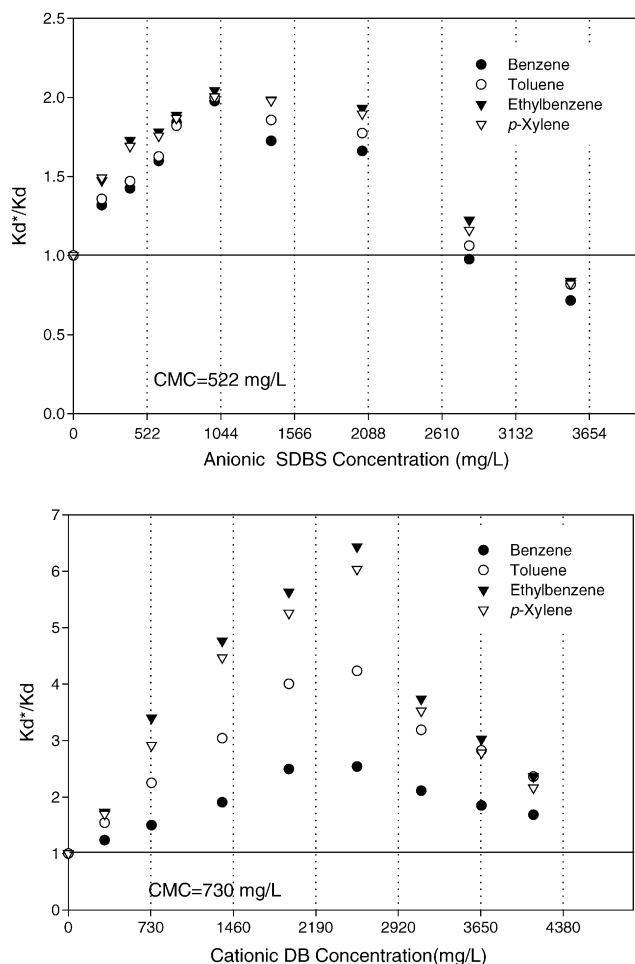


Fig. 2. Changes in K_d^*/K_d values of BTEX on SMS with SDBS and DB at the various added surfactant concentration.

K_d^*/K_d until the surfactant forms micelles in the liquid phase, which promotes the release of contaminants from soils. On the other hand, the cationic surfactant molecules aggregate readily on the soil mineral surface to form admicelles, with a weak partitioning into the SOM. The point of decline for this K_d^*/K_d goes beyond the maximum surfactant uptake on the soil surface. The basic assumption for admicelles is that the adsorption of surfactants at the solid/liquid interface generally occurs in two steps [21]. In the first step the surfactants are adsorbed as individual ions or molecules in the first layer of the solid surface through electrostatic attraction (this applies only for cationic surfactants) and/or specific attraction (e.g., hydrogen bonding between surfactants and mineral surface). In the second step the adsorption increases dramatically, as the admicelles form on the adsorbent through association or hydrophobic interactions between the hydrocarbon chains of the surfactants. Eq. (3) explains this phenomena that $(1 + f_{sf}K_{sf}/K_d) > (1 + X_{mn}K_{mn} + X_{mc}K_{mc})$ holds until the contaminants exceed the apparent S_w . For the different f_{om} soils, the TCS will have a relatively higher SA and a lower CEC than the SMS, which complicates the saturation capacity of the adsorbed surfactant. This result must be discussed further.

Contaminant desorption in the surfactant-soil-water system is dependent on the hydrophobic surfactant solution, i.e. $(1 + X_{mn}K_{mn} + X_{mc}K_{mc}) > (1 + f_{sf}K_{sf}/K_d)$. As mentioned earlier, the steps for admicelle formation are that surfactants reach a saturated monomeric adsorption on the mineral surface, and then the surfactants act as a bridge to connect other surfactants via van der Waals forces or hydrogen bonds. Accordingly, the high surfactant amounts adsorbed by the soil (higher f_{sf}), held in the first layer, cause the higher CMC values in the solution. This is the reason why higher surfactant amounts need to be added to the solution to obtain the same soil remediation efficiency. The results indicate that anionic surfactants are more effective for removing contaminants from soils.

4.2. Effects of the soil properties

Whereas an electronic interaction results in an obvious difference in the desorption of contaminants from soil between cationic and anionic surfactant systems, the effects of the soil properties on the BTEX desorption by the surfactants cannot be clearly stated. Nonionic surfactants should be a good reference to discuss the effects of the soil properties on organic contaminant desorption because of their weak interactions with soils. Indeed, the obvious f_{om} and SA difference can be used to further elucidate the effects. Generally, the nonionic surfactant sorption on soils is correlated mainly with the composition of the mineral phase on which the desorption of the contaminants is similarly dependent [15,21]. However, for FP, a soil with a high SOM content ($f_{om} = 0.864$) and a low-SA value ($SA=1.30 \text{ m}^2/\text{g}$) probably has a significant TX-100 partitioning to the SOM [9]. Fig. 3 illustrates the changes in K_d^*/K_d ratio for the BTEX, for a wide range of nonionic surfactant concentrations and for two soils with a low and a high f_{om} . The striking differences are as follows: (i) the FP has a lower K_d^*/K_d than does the TCS; (ii) the K_d^*/K_d ratios for the BTEX on the FP are approximate, and on the TCS are slightly inversely proportional to the S_w of the BTEX; (iii) for the FP, the K_d^*/K_d ratios sharply increase if the surfactant concentration is below CMC, but exhibit a “slow rise” when the surfactant concentration above CMC to the given TX-100 concentration; (iv) for the TCS, the top value of the ratio is two to three times is the CMC, at which point the ratio declines as the surfactant concentration increases. The above results may be rationalized with the soil properties. As mentioned above, nonionic surfactants adsorbed to low f_{om} soils are mainly correlated with the mineral properties of a soil. The TCS with a relatively higher soil mineral fraction reasonably adsorbs a greater amount of surfactant, to which the contaminants can partition, on the soil surface leading to an obvious increase in the K_d^*/K_d ratios. On the other hand, since the BTEX compounds are relatively water soluble ($S_w > 100 \text{ mg/L}$), the solubility enhancement effects of the surfactant in the solution are weak. This means that the surfactants adsorbed on the soil surface may be the predominant factor determining the K_d^*/K_d values. As TX-100 surfactant par-

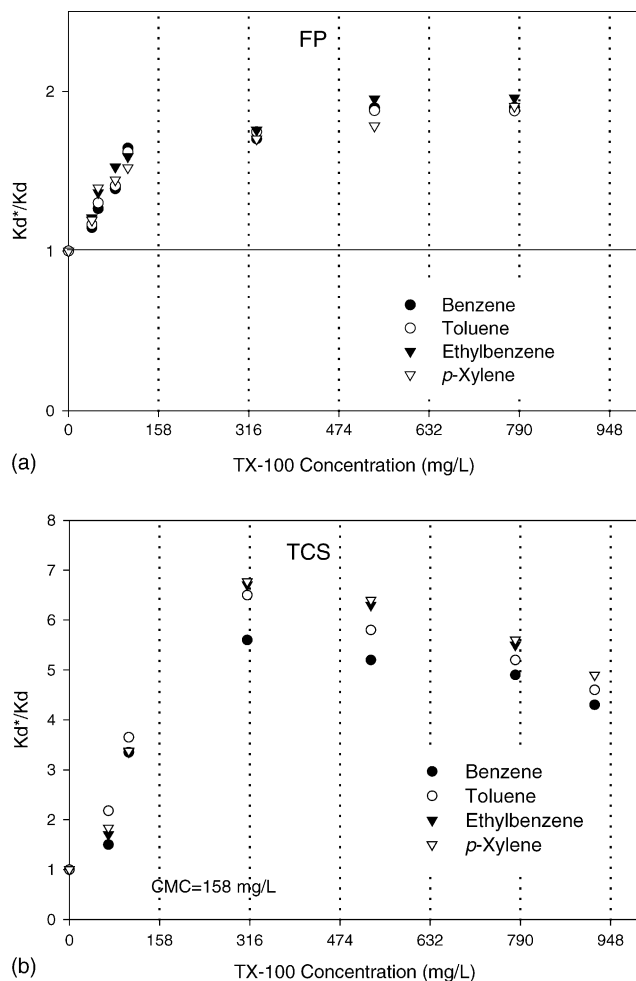


Fig. 3. Changes in K_d^*/K_d of BTEX on FP and TCS with the various added TX-100 concentration (CMC = 158 mg/L).

tioning into the SOM cannot form admicelles, the BTEX compounds partitioned mainly onto the FP organic matter [9]. The hydrophobic properties of BTEX with respect to the SOM are similar. In spite of the obvious K_d diversity, the SOM effects (K_d^*/K_d) relative to the water soluble and similar structure BTEX are expected to be identical. For the TCS, since the BTEX compounds partition onto the adsorbed surfactant and SOM, the observed K_d^*/K_d ratio is a result of competition between the surfactant adsorbed onto the soil and that dissolved in the solution. When surfactant monomers exist in the solid phase, the effect of the sorbed surfactant on the solute uptake (i.e., $f_{sf}K_{sf}/K_d$) should be about the same for all solutes because K_{sf} should be largely linearly related to K_{om} . In Eq. (3), similar K_{sf} values lead to approximate changes in the K_d^*/K_d ratios under the given surfactant concentrations. When the surfactant increases continuously to form admicelles on the soil surface, the BTEX compounds partition into the admicelles, indicating the different K_{sf} values to cause the K_d^*/K_d difference. As mentioned earlier, the major factor of influence for K_d^*/K_d values is the surfactant on the soil, that is $f_{sf}K_{sf}/K_d$ term. It is well known that lower

S_w compounds (e.g. ethylbenzene) have a higher K_d^* to result in a slightly higher K_d^*/K_d . If we compare the nonionic TX-100 with the cationic DB, we see a similar result that the cationic surfactant can also form admicelles, and this can cause the diversity in the K_d^*/K_d for the BTEX compounds under the given surfactant concentrations (see Figs. 1 and 2).

As the surfactant is adsorbed onto the soil, the SOM significantly enhances until the adsorption capacity approaches saturation. This leads to a dramatic rise in the K_d^*/K_d prior to the adsorption saturation. However, as the solid f_{om} increases, the amount of “adsorbed” surfactant on the mineral matter may decrease, which could then reduce the impact of the surfactant on the solute uptake. For the FP, the SOM effect is greater than the surfactant effect. Thus, the K_d^*/K_d curves do not drop significantly within the given surfactant concentration range. As for the TCS, the reason for the drop in the K_d^*/K_d curves may be consistent with the reason mentioned above that the surfactant forms micelles in the solution, thus increasing the affinity of the BTEX compounds to the solution. The slow drop in the curves means that the effects of the soil properties on the desorption of water soluble compounds are higher than the solution properties. The obtained results reveal that nonionic surfactants have difficulty removing water soluble compounds from high-SOM soils, and high surfactant concentrations are needed to remedy low-SOM soils.

4.3. Effects of solute S_w

Given the reasoning above, the K_d^*/K_d values for different solute desorption would be expected to vary with the solute S_w . To focus on the difference that S_w makes on the effective soil remediation, the K_d^*/K_d changes corresponding to the three low- S_w pesticides in two soils and TX-100 mixtures are illustrated in Fig. 4. A number of desorption characteristics are mentioned below. (i) All of the ratios are less than one, and also decrease as the surfactant concentration increases. (ii) An obvious reduction in the ratio exists at the CMC point and then shows a tendency to decline smoothly under excessive CMC values. (iii) The K_d^*/K_d ratios for the three pesticides are quite approximate when the surfactant concentrations are below the CMC, but obviously different when the surfactant concentrations are above the CMC. (iv) The K_d^*/K_d values are inversely proportional to the aqueous solubility of the selected compounds. (v) The K_d^*/K_d values for the FP are lower than those for the SMS.

In Eq. (3), $K_d^*/K_d < 1$ indicates that the denominator term is greater than the numerator term, which can be logically ascribed to their greater ($X_{mn}K_{mn} + X_{mc}K_{mc}$) values, because of their relatively low S_w . The solution properties are the dominant factor for the desorption of low- S_w compounds from contaminated soils with the SOM contents. As the surfactant forms micelles in the solution, these offer a better hydrophobic environment, which attracts contaminants released into the solution. In the water phase, the surfactant effect on the apparent solute solubility, from Eq. (2), i.e.,

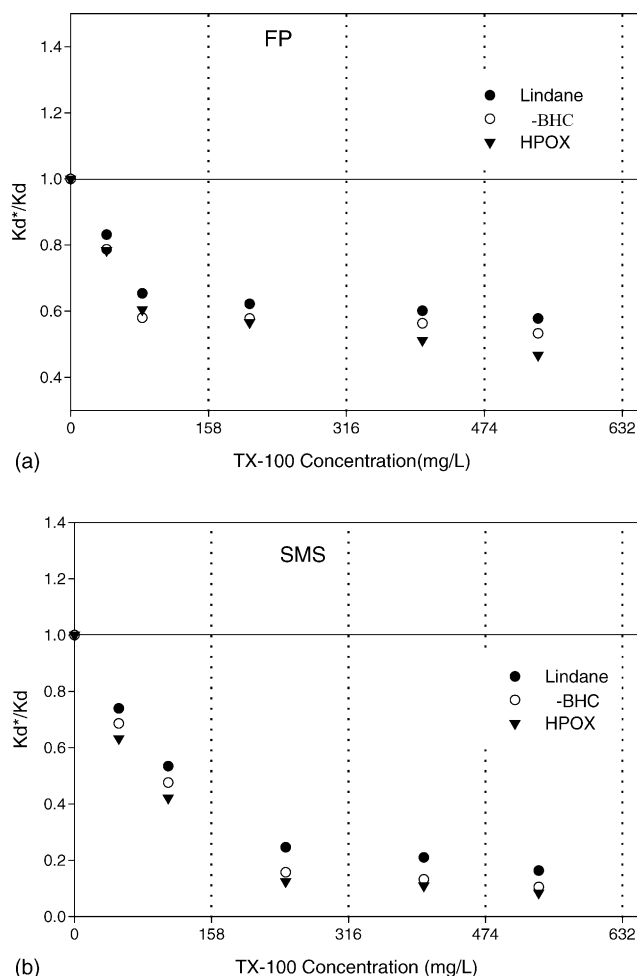


Fig. 4. Changes in K_d^*/K_d of low- S_w pesticides on FP and SMS with the different with the various added TX-100 concentration (CMC = 158 mg/L).

$(1 + X_{mn}K_{mn} + X_{mc}K_{mc})$, is known to increase sensitively with the K_{ow} or $1/S_w$ of the solute. Knowledge of when the surfactant concentration reaches the CMC can significantly enhance the apparent S_w of the less water soluble compounds e.g. trichlorobenzene [7]. This obvious reduction in the K_d^*/K_d values is easy to understand on the basis of solubility enhancement. For this reason, a more significant K_d^*/K_d difference occurs when the surfactant forms micelles. This also leads to the lower S_w . HPOX generates the relatively lower K_d^*/K_d . On the other hand, although the surfactant concentration exceeds CMC, the obvious K_d^*/K_d reduction cannot be found. This may also result from difficult desorption of three pesticides from SOM. This reason is the high affinity between the NOCs and the SOM, which is the same as the BTEX desorption from the FP. Thus, K_d^*/K_d values of three pesticides on the FP are higher than those on the SMS at the given surfactant concentration. The obtained results of the $K_d^*/K_d < 1$ can still demonstrate that the relatively less water soluble compounds (e.g. the pesticides) can be more effectively washed from contaminated soils, especially for a low-SOM soil.

5. Conclusions

In this research, Eq. (3) was applied to evaluate the efficiency of soil remediation for different S_w compounds with various surfactant solutions. The anionic surfactants are preferable for soil remediation due to little adsorption on the soil surface, which leads to easy micelle formation in the solution, causing the contaminants to be released from the soil. Cationic surfactants may adsorb onto the soil surface to form admicelles in which contaminants can partition. This leads to difficulty in obtaining good remediation efficiency unless a very high surfactant concentration is used. The affinity of NOCs to the SOM is beyond that to the adsorbed surfactants. Although nonionic surfactants adsorb on the soil mineral surface of the soil, which may also hinder the contaminant desorption, the contaminant partitioning to the SOM can lead to an increased difficulty in soil remediation, especially for the water soluble compounds. This indicates that surfactant washing of low-SOM soils should produce better remediation efficiency under the same conditions. For different S_w compounds, the primary sorptive effects of the relatively water soluble compounds are due primarily to the soil properties. For the less water soluble compounds, they are due to the solution properties. Surfactant washing can be used for effective soil remediation because of an increase in the hydrophobic environment of the solution. In summary, the best choice for soil remediation by surfactant washing is composed of the lower SOM in the soils, the lower polarity of the surfactants (either anionic or nonionic), and the low- S_w contaminants.

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